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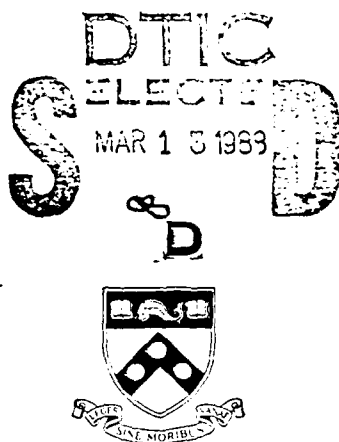
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FIFTH QUARTERLY R&D STATUS REPORT

Principal Investigator:
Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania

REPORTING PERIOD: 10/1/87 - 12/31/87

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UNIVERSITY of PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA 19104

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ARPA ORDER NO.: a400004df301
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CONTRACTOR: Trustees of the University of Pennsylvania
Office of Research Administration
Suite 300 Mellon Building
133 S. 36th Street
Philadelphia, PA 19104-3246

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OF CONTRACT: 9/15/86

EXPIRATION DATE
OF CONTRACT: 9/14/91

TELEPHONE NO.: 215-898-8307 or 215-898-6323

SHORT TITLE OF WORK: **Conducting Electronic Polymers by
Non-Redox Processes**



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I. Research Groups*

1. University of Pennsylvania
 - (a) Department of Chemistry (A.G. MacDiarmid)
 - (b) Department of Materials Science (G.C. Farrington)
2. The Ohio State University
Department of Physics (A.J. Epstein)
3. Lockheed Advanced Aeronautics Corporation
Aeronautics Systems Group Research (T.S. Kuan)
4. Rensselaer Polytechnic Institute
Department of Chemistry (G.E. Wnek)
5. University of Rhode Island
Department of Chemistry (S.C. Yang)
6. Montclair State College
Department of Chemistry (B.D. Humphrey)



per call J.C.

A-1

*Financial information for each group given in Section IX.

II. Description of Progress

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)†

(i) Summary of Progress

Segmented Polyacetylene, (CHD_y)_x: Electrochemical n-Doping Studies*

Defects involving sp³ hybridized carbon atoms in the form of (HCD) units have been controllably introduced into *trans*-(CH)_x by chemical methods to produce polymers of the type *trans*-(CHD_y)_x, i.e., [(CH)_{1-y}-(HCD)_y]_x (y=0, 0.15 and 0.17), in order to study the nature of these defects and their effect on the electronic and magnetic properties of *trans*-(CH)_x. The effects of these defects on the electrochemical reduction (n-doping) of *trans*-(CHD_y)_x up to 4.0 mol % reduction levels have been studied. The results are consistent with optical and Raman spectra of *trans*-(CHD_y)_x species and are interpreted as showing that: (i) the band gap in *trans*-(CHD_y)_x is essentially unchanged from that in *trans*-(CH)_x because of a small but significant amount of long conjugated sequences remaining in the deuterated polymer; (ii) the maximum density of states near the conduction band edge has moved upwards from the band edge; and (iii) the (HCD) defects are clustered rather than randomly spaced in a given (CHD_y)_x chain.

*Supported in part by URI and by NSF Grant No. DMR-86-15475 and ONR Grant No. N-00014-83-K-0209.

Highly Conducting Polyacetylene*

"New"-(CH)_x and "ARA" (i.e. Additional Reducing Agent)-(CH)_x have been synthesized at room temperature. "New"-(CH)_x is formed by polymerizing acetylene on flat polymeric or glass substrates using an AlEt₃/Ti(n-BuO)₄ catalyst in silicone oil which has previously been heat-treated. Additional reducing agents may be added to the catalyst after its thermal treatment to produce "ARA"-(CH)_x. The stretch-oriented "New"-(CH)_x polymerized on glass and "ARA"-(CH)_x polymerized on polyethylene can be p-doped with I₂/CCl₄ to give conductivities of ~50,000 and ~75,000 S/cm

†In collaboration with Professor A.J. Epstein, Department of Physics, The Ohio State University.

respectively. Optical absorption, photoinduced, infrared absorption, magnetic susceptibility and conductivity studies on selected forms of the above doped and undoped types of $(CH)_x$ have been studied. The electronic structure of highly conducting "New"- and "ARA"- $(CH)_x$ is observed to be essentially identical to that of conventional Shirakawa- $(CH)_x$.

*Supported in part by URI and by NSF Grant No. DMR-85-19059.

^{15}N NMR of Polyaniline*

^{15}N NMR spectroscopy has been utilized as a structural probe for the leuco- and "emeraldine" base forms of polyaniline. Preliminary results suggest that the emeraldine base polymer exists as an alternating copolymer of oxidized and reduced units. End-groups are not detected at the experimental level of sensitivity.

*Supported in part by URI and by NSF Grant No. DMR-85-19059 and by NIH Grant No. GM-24266.

(ii) Major Equipment Purchased or Constructed

A PhotoResist Spinner for casting films was purchased.

b. Department of Materials Science and Engineering (Farrington)

Summary of Progress

Jonathan Foreman continues his investigations of the reductive (n-doping) electrochemistry of polyacetylene with a focus on the new oriented and ultrapure forms of the material prepared by Nick Theophilou.

Hong Yang has found that network PEO takes up a far smaller concentration of divalent cation salts than linear PEO. This could either be the result of unfavorable partition of the salt between the non-aqueous solvent used to dope the PEO or of some more fundamental structural difference between linear PEO and the network form which leads to less favorable divalent cation solvation in the network form. Either way, the result is intriguing and will be pursued. Hong Yang is also continuing her studies of linear PEO electrolytes containing Zn(II). These materials are particularly interesting because of their potential application as Zn(II) conductors in high energy density batteries.

2. The Ohio State University

Department of Physics (Epstein)‡

(i) Summary of Progress

The conductivity of the metallic emeraldine salt polymer is sensitive to the environmental humidity. Travers and Nechtschein have proposed the presence of a conduction mechanism based on electron hopping between localized states, with a proton exchange-assisted conduction of electrons (PEACE). Last quarter, we discussed room temperature studies of the frequency dependence of the conductivity of the range of dc - 10^{10} Hz as a function of exposure to room atmosphere and dynamic pumping. The conductivity of the protonated emeraldine is independent of frequency, even though this range of frequency spans from below to above the frequency for proton exchanges in the polymer. These results show that the PEACE mechanism is not appropriate for the emeraldine salt polymer. We have monitored the temperature dependence of the four-probe conductivity of emeraldine salts before and after pumping for a period of twenty hours. The after pumping data is in agreement with our earlier reported σ (300K) ~ 0.2 S/cm and $T_0 = 7800$ K where $\sigma \equiv \sigma_0 \exp(-(T_0/T)^{1/2})$. The data for the sample without evacuation before cooling shows a higher conductivity at room temperature ($\sigma(300\text{K}) \sim 1$ S/cm) and a similar temperature dependence with a much weaker slope $T_0 = 1400$ K. These results are interpreted in terms of the continued presence of barriers between granular metal islands. These barriers are reduced with the absorption of moisture. Hopping between random sites within each metallic island would contribute to excess microwave conductivity with respect to dc at low temperatures, when transfer between islands is very difficult.

The conductivity measured at microwave frequencies (6×10^9 Hz) decreases by a similar factor upon pumping of the sample. Although the conductivity changes by a factor of five upon pumping, there is a slower variation of dielectric constant with pumping, decreasing by only twenty-five percent between zero time and a five minute pump, and achieving an asymptotic value, (reduced by a factor of two), after an eight hour pump. Though the microwave conductivity is dominated by links between conducting grains with the smallest

‡In collaboration with Professor A.G. MacDiarmid, Department of Chemistry, University of Pennsylvania

barriers, the dielectric constant is a measure of the capacitance of the entire sample. The continued decrease in the dielectric constant when pumping beyond five minutes suggest that most of the barriers between the conducting grains continue to widen or a new barrier is developed within the conducting grains as the moisture decreases. Localization of the absorbed water molecules could not account for the excess dielectric constant of unpumped samples, indicating that the large increase of dielectric constant with exposure to moisture is electronic in origin. Comparison of the results for T_0 with predictions of models of very strong localization in disordered systems (Efros and Shklovskii; Nemeth and Muhlschlegel) show that these analyses for strong localization do not produce quantitative agreement with our data. Using a model of Sheng and Klafter (Phys. Rev. B 27, 2583 (1983)) values for the tunneling parameter in charge energy limited tunneling are estimated.

Our photoinduced absorption studies of emeraldine have been extended to the infrared regime. Initial studies have been carried out on emeraldine on wire grid, emeraldine thin films cast on KBr, and emeraldine powder dispersed in KBr in the form of pressed pellets. Careful measurements are being made to isolate thermal effects from photoinduced absorption effects. We note that the details of the photoinduced spectra depend upon the sequence with which the data are taken. Similarly we have been extending our photoinduced absorption studies in the near-IR through UV solutions of emeraldine. Again, heating effects seem to be an important component and care has been taken to separate these effects out.

Susceptibility is being measured on fully and partly methylated emeraldine. For emeraldine base pseudoprotonic acid doped with dimethylsulfate, there is an increase in the susceptibility with increasing doping. The fifty percent doped polymer (in principal, all-N=sites reacted with a CH_3^+) has a Curie susceptibility corresponding to 8.0×10^{-2} spin/2 rings (approximately four times that of emeraldine salt). The Pauli susceptibility, χ^P , of emeraldine increases linearly with $(\text{CH}_3)_2\text{SO}_4$ doping, with the increase being approximately half that of the increase of χ^P upon doing with the equivalent amount of HCl. These data suggest a significantly greater contribution from a bipolaronic form in the methyl-doped polymer as compared with the proton-doped material, likely due to the translational symmetry breaking effects of the methyl group.

In order to understand the nature of localized excitations within quasi-two-dimensional structures in the presence of large Coulomb interactions, we have carried out photoexcitation studies in the La_2CuO_4 . Two photoinduced absorptions were observed, peaking at 0.5 and 1.4 eV, with a crossover to photoinduced bleaching above 2.0 eV. The intensity of the absorption in

bleaching bands decreases with increasing temperature with a similar temperature dependence. The intensity of the photoinduced absorption in bleaching bands is roughly proportional to the square root of the incident laser power, indicating a bimolecular type decay, though the chopping frequency behavior indicates the two photoinduced absorption peaks differ. The data, together with the first report of luminescence at ~ 2 eV, confirm the presence of an energy gap of ~ 2 eV, as well as the existence of long-lived stable electronic defect states in this system. The photoinduced absorption peaks may reflect the presence of soliton, polaron or bipolaron type defects within the cuprate lattice similar to the presence of photoinduced defects in polymers, such as polyacetylene or polyaniline. In parallel with our studies in polyaniline, the absence of charge conjugation symmetry in the cuprate system suggests that the two absorptions at 0.5 eV and 1.4 eV peaks are not the two bipolaronic levels of a single charge defect within the layered electronic structure.

(ii) Major Equipment Purchased or Constructed

The picosecond optical apparatus has been installed and experiments have begun on this system. We have received the following items: a potentiostat/galvanostat, a pulse generator, and a coulomb meter for electrochemistry experiments; a programmable current source; and a vacuum shroud for a continuous flow liquid helium refrigerator. We have constructed a liquid nitrogen cold finger to be used with the vacuum shroud. Miscellaneous optical and electrical components were purchased. Optical fibers were purchased for use with FTIR and EPR equipment to coordinate with photoinduced IR and electron spin resonance studies.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Summary of Progress

Continued effort was directed towards understanding the thermal decomposition pathway of conductive polyaniline as well as methods to stabilize the material. An increase in the thermal stability of these materials is essential to meet the needs of many electronic applications. FTIR, UV-Vis and dielectric studies of the polyaniline during heating were performed to analyze this decomposition for various polyaniline derivatives. Polyaniline derivatized with very stable and nonvolatile acids still seems to yield the most thermally stable conductive polyaniline. A paper concerning these studies is being prepared.

Alignment of polyaniline was attempted in liquid crystalline solvents. These studies were initiated in an effort to perform optical and electronic polarization studies of the polyaniline. Unfortunately, the polymer was not found to be soluble in most liquid crystals used. Some success was found with a 50:50 mixture of EBBA:MBBA which is a nematic liquid crystal at room temperature. Although the polyaniline free base is not soluble in this, we found that if o-sulfobenzoic anhydride is first added to the liquid crystal, the polyaniline is a little more soluble in the "solution." Since EBBA:MBBA is yellow and thus transparent to a portion of the visible spectrum, a visible optical polarization spectra of the polyaniline was obtainable. Furthermore, since the o-sulfobenzoic anhydride reacts slowly with the polyaniline, the transition from the emeraldine free-base to the conductive polyaniline state could be monitored while the polyaniline is aligned in the liquid crystal. Further studies will be performed to obtain cleaner spectra. Higher solubility of the polyaniline in the conductive polymer would be ideal. However, these studies do reveal that the polyaniline can be aligned. Furthermore, these studies open up the possibility of performing detailed optical studies of the chemical derivatization of polyaniline.

During 1987 we found that polyaniline free base can be photochemically derivatized with tungsten pentacarbonyl. We are beginning work on using this type of technology to control the derivatization of polyaniline. Films of the polyaniline free base are coated with a film of tungsten hexacarbonyl. Areas of the film which are exposed to 313nm light undergo derivatization with the photoinduced tungsten pentacarbonyl. Consequently conductive patterns may be produced onto the film surface. Although this process is at a very young stage, and tungsten carbonyl may not be the optimum acid precursor, the use of a photosynthesized acid to derivatize polyaniline emeraldine free-base films may prove to be an easy method of producing microscopic electronic circuits or films with geometrically contoured conductivities.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Summary of Progress

Renovations to Professor Wnek's laboratory at RPI are almost complete and experiments are already in progress. A first-year graduate student, Lynette Prezyna, has joined the group and will be supported by the URI program. Her work will focus protein binding to conducting polymers, including polypyrrole and polyaniline. The objectives are (1) to demonstrate reversible

binding of proteins as a function of electrochemical potential, and (2) understand the mechanism of binding (i.e., what portion(s) of the protein bind to the conducting polymer and why). Initial experiments are focusing on poly(pyrrole)/poly(styrenesulfonate). The protein of interest is histone H3, one of the DNA-binding proteins of chromosomes.

Work on functionalization of polyacetylene using charge carriers as reactive intermediates is also continuing. Our goal is to develop methodology for the covalent attachment of biologically active macromolecules to polyacetylene film surfaces. Also, we are continuing to address the question of homogeneity of defect placement in upon protonation or alkylation of n-type polyacetylene. A collaboration with Professors S. Clough and S. Tripathy at the University of Lowell on theoretical aspects of defect placement is underway.

5. University of Rhode Island

Department of Chemistry (Yang)

Summary of Progress

The objectives for this second year of research are: (1) Morphological modification of polyaniline. (2) Kinetics of the electrochemical doping process. (3) Development of the electrochemical-optical-EPR triple hybrid spectroscopic technique to study the correlation between the doping induced electronic structure transformation with the doping induced transformation of electron spin states.

Our financial situation has been difficult in this quarter. We have no unspent funds from last year to relieve problems associated with the funding gap of this year. The third project listed in the above is delayed because it depends on equipment to be purchased under this year's budget.

We were, however, able to make considerable progress in the first and the second objectives. These works are partially supported by an industrial grant. The following is a brief description of work done in these two areas:

Morphological modification of polyaniline:

The objective of this study is to find a systematic method to modify the morphology of polyaniline. Polymer morphology is the manifestation of the microscopic structural arrangement and the aggregation of polymer molecules. The morphology of conducting polymers may have strong influence on its

electrical conductivity and the rate of chemical transformation in response to electrochemical doping. These properties are important to the use of polyaniline as a reversibly switchable optical or electrical materials.

The central idea for morphological modification involves the use of molecular templates to pre-arrange the relative alignment of the aniline monomers before the polymerization takes place. The conducting polymer formed will then have a morphology dictated by the specific interactions of the template molecules. The template molecules that we explored are polymer electrolytes that have a variety of modes of binding with the aniline monomer. Examples are polyacrylic acid, polyvinylsulfonic acid, polystyrene sulfonic acid. Our electron microscopy study indicated that polyaniline morphology is strongly influenced by the choice of template molecules.

Kinetics of the electrochemical doping of polyaniline.

The kinetics was studied by recording the optical absorption spectra as a function of time after the electrochemical doping or undoping. We found that the transformations induced by small steps of electrochemical doping follow first order kinetics and can be decomposed into one fast process and one slow rate process. The kinetics was studied as a function of the electrochemical potential and the pH of the electrolyte solutions. A kinetics-based pH-potential phase diagram was constructed.

6. Montclair State College

Department of Chemistry (Humphrey)

Summary of Progress

During the fifth quarter in depth spectroscopic studies of polyaniline/polysaccharide composites were carried out as a function of solution pH. These studies in conjunction with earlier electrochemical/pH studies conclusively demonstrate that the presence of the conducting polymer (polyaniline in this set of investigations) is responsible for the conductivity and spectroscopic properties exhibited by these composite materials. This information was necessary to gain a complete picture as to the nature of these new composites. This was also the final information necessary for publication concerning these materials and a manuscript describing these systems and their properties is being prepared for submission to Synthetic Metals.

These studies also demonstrated the viability of using these materials as inexpensive, reusable optical pH sensors over the range pH=3 to pH=7. This is a wide range of pH to be covered by a single material, however, this range can even be extended further by including conductivity pH sensitivity (perhaps to pH=-2). A combination sensor based upon these properties would be easy to construct, have a fairly rapid response, and could be used repeatedly with reliability.

In addition to these studies, further work was completed on the synthesis of conducting rayon thread using these composite materials. Both the cuprammonium process and the carbon disulfide viscose process appear viable as demonstrated by dissolving samples of polyaniline/cellulose and polypyrrole/cellulose then regeneration of these materials as rayon fibers. This is accomplished by extruding the dissolved cellulose materials in dilute acid.

III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

1. October 14-15, 1987, Subcontractor's meeting held at University of Pennsylvania. A.G. MacDiarmid and his entire group attended together with G.C. Farrington, J. Foreman and R. Huq of MSE, A.J. Epstein, and R. McCall of OSU, R. Cameron of Lockheed, G. Wnek and L. Prezyna of RPI, and S.C. Yang of Rhode Island.
2. October 16, 1987, Dr. S.C. Yang visited the laboratory of Dr. A.G. MacDiarmid.

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. October 1-13, 1987, Professor Xin Sun, Fudan University, Shanghai, The People's Republic of China, visited Dr. Epstein's lab at Ohio State University. Title of talk given: "The Effect of Electron Interaction on the Bond Alternation of Polymers."

2. Oct 4-7, 1987 - Dr. A.G. MacDiarmid gave an invited lecture at the Symposium on Electroresponsive Polymers at Brookhaven National Labs, Upton, NY (Brookhaven Symposium). Title of the talk given: "The Polyanilines: A New Concept in Conducting Polymers."
3. Dr. A.J. Epstein also gave an invited lecture at the Brookhaven Symposium entitled "Polaronic Defect States in Polyaniline."
4. Anjan Ray of Dr. MacDiarmid's group presented a poster at the Brookhaven Symposium entitled "Electrochemistry of Ring-Substituted Polyanilines." Co-authors were Dr. Alan MacDiarmid of the University of Pennsylvania and Dr. Yen Wei, Walter Focke, and Dr. Gary Wnek of RPI.
5. Marie Angelopoulos of Dr. MacDiarmid's group presented a poster at the Brookhaven Symposium entitled "Pseudo-Protonic Acid Doping of Polyanilines." Co-authors were Susan Ermer, Sanjeev Manohar, Dr. Alan G. MacDiarmid of the University of Pennsylvania and Dr. Arthur J. Epstein of OSU.
6. Hamid Javadi of Dr. Epstein's group presented a poster at the Brookhaven Symposium entitled "Frequency Dependent Conductivity of Emeraldine: Absence of Protonic Conductivity." Co-authors were Fulin Zuo and Arthur Epstein of OSU and Marie Angelopoulos and Alan MacDiarmid of the University of Pennsylvania.
7. October 8, 1987, Professor Jean-Luc Bredas, Department of Chemistry, University of Notre Dam de la Paix, Namur, Belgium, visited Dr. Epstein's lab at Ohio State University. Title of talk given: "New Perspectives on Electronic Structure of Conducting Polymers: Polythiophene and Polyacetylene."
8. October 9, 1987, Dr. Jean-Pierre Travers of the Centre d'Etudes Nucleaires de Grenoble, France, visited the laboratory of Dr. A.G. MacDiarmid. Title of talk given, "Recent Developments on Polyaniline Studies."
9. October 12, 1987, Dr. Jean-Luc Bredas of the Universitaires Notre Dame de la Paix, France, visited the laboratory of Dr. A.G. MacDiarmid. Title of the talk given, "Electronic Structure of Conjugated Polymers."
10. October 12, 1987, Dr. J.P. Travers, Centre Detudes Nucleaires De Grenoble, Grenoble, France, visited Dr. Epstein's lab at Ohio State University. Title of talk given: "Recent Developments on Polyaniline Studies."

11. October 22-23, 1987, Dr. Epstein Visited DuPont to meet with Dr. Joel Miller.
12. October 29, 1987, Dr. Epstein presented a talk entitled "Polaron and Bipolaron Defects in Polymers: Polyaniline" at the Colloquium of the Department of Physics, University of Kentucky, Lexington, KY.
13. November 1, 1987, Dr. G.E. Wnek attended the ACS Southeast Regional Meeting, Orlando, FL, invited talk given "Electrically Conducting Polymers: New Chemistry and New Applications."
14. November 2, 1987, Dr. A.G. MacDiarmid gave an invited lecture at the International Symposium on the Development of Conducting Organic Polymers and Ultra-thin Films and Their Uses in Electronics, Stockholm, Sweden, entitled "Polyaniline: A New Concept in Conducting Polymers."
15. Professor Roger Linford of Leicester England spent two months (November 1st - December 30th) visiting the laboratory of Professor G.C. Farrington investigating solid polymer electrolytes as part of an on-going collaboration.
16. November 9 1987, Dr. Keith Wilbourn, University of Massachusetts, Amherst, MA, visited Dr. MacDiarmid's laboratory. Title of the talk given: "Chemistry and Electrochemistry of BBL - an Analog of Aniline."
17. November 9, 1987, Dr. Epstein attended the 32nd Conference on Magnetism and Magnetic Materials in Chicago, IL.
18. November 10, 1987, Dr. Mark Thompson, Princeton University, NJ, visited Dr. MacDiarmid's laboratory. Title of the talk given: "Synthesis of Organometallic Compounds by Intercalation."
19. November 10, 1987, Dr. Epstein attended an organizational meeting of the International Conference on Science and Technology of Synthetic Metals at Los Alamos, NM.
20. November 10-December 4, 1987, Dr. Epstein, John Ginder, and Fulin Zuo (expenses paid by other sources) attended the Material Research Society Conference in Boston, MA.
21. December 11, 1987, Dr. Epstein presented a Visiting Scholars/Sigma Xi Lecture entitled "Frontiers in Polymers: Polaron Defects in Polyaniline" in the Department of Physics and Chemistry at the University of Rhode Island, Kingston, RI.

22. December 16-17, 1987, Dr. Epstein met with Dr. Joel Miller at DuPont to discuss plans for a joint polymer program.

23. December 21-22, 1987, Dr. Joel Miller of DuPont visited Dr. Epstein's lab at Ohio State University. Title of talk given: "Molecular and Polymeric Ferromagnetism."

V. Publications

Papers Accepted/Submitted for Publication

(i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Protonation of Emeraldine: Formation of a Granular Polaronic Polymeric Metal," Mol. Cryst. Liq. Cryst., in press (1987), A.J. Epstein and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Frequency Dependent Conductivity of Emeraldine: Absence of Protonic Conductivity," Mol. Cryst. Liq. Cryst., in press (1987), H.H.S. Javadi, F. Zuo, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

"Pseudo-Protonic Acid Doping of Polyaniline," Mol. Cryst. Liq. Cryst., in press (1987), M. Angelopoulos, S.P. Ermer, S.K. Manohar, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059 and in part by NASA Grant No. NAG-10-0025).

"Polyaniline: Solutions, Films and Oxidation State," Mol. Cryst. Liq. Cryst., in press (1987), M. Angelopoulos, G.E. Asturias, S.P. Ermer, A.Ray, E.M. Scherr, A.G. MacDiarmid, M. Akhtar, Z. Kiss and A.J. Epstein. (Supported in part by URI and in part by NSF Grants No. DMR-85-19059 and DMR-86-15475).

"Segmented Polyacetylene, $(\text{CHD}_y)_x$: Electrochemical n-Doping Studies," Synth. Met., in press (1987), M.X. Wan, G.A. Arbuckle, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by ONR Grant No. N00014-83-K-0209 and in part by NSF Grant No. DMR-86-15475).

"Polyaniline: A New Concept in Conducting Polymers," International Symposium on Development of Conducting Organic Polymers and Ultra-Thin

Films and Their Use in Electronics, Stockholm, Sweden, November 2, 1987, in press, A.G. MacDiarmid. (Supported in part by URI and in part by ONR Grant No. N00014-83-K-0209 and in part by NSF Grants No. DMR-82-16718 and DMR-85-19059).

(ii) Wnek, MacDiarmid, Epstein (RPI/Penn/OSU)

"Electrochemistry of Ring Substituted Polyanilines: Effect of Substituents on Electronic Properties," Mol. Cryst. Liq. Cryst., in press (1987), A. Ray, J.C. Chiang, A.G. MacDiarmid, Y. Wei, W.W. Focke, G.E. Wnek and A.J. Epstein. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059).

VI. Patents

Patents resulting from URI support

None

VII. Changes in Personnel

1. University of Pennsylvania

a. Department of Chemistry (MacDiarmid)

Georgia Arbuckle graduated with her Ph.D. on December 4, 1987. The title of her thesis is "Polyacetylene: Relationship Between Electronic, Optical, and Magnetic Properties and Conjugation Length." She was supported by the URI from 9/87 to 12/87. She took up a post-doctoral position with Professor A. B. Bocarsly, Department of Chemistry, Princeton University.

Dr. Nicholas Theophilou, expert in highly conducting polyacetylene, joined Dr. A.G. MacDiarmid's group on December 16, 1987.

b. Department of Materials Science and Engineering (Farrington)

There was no change in personnel this quarter.

2. The Ohio State University

Department of Physics (Epstein)

Cheryl Sievert was employed as an undergraduate aid to assist with secretarial responsibilities.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Ms. Margaret Reed has terminated her employment with the Lockheed Aeronautical Systems Company. She will soon begin work as an analytical chemist with the Atlantic Richfield Company in Alaska. Mr. John Beale will be replacing her position in our analytical group.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

Lynette Prezyna has joined the group of Dr. Gary Wnek. After the first year of graduate studies, when she will be taking courses and fulfilling her teaching obligations, she will begin full time research in the Spring of 1988.

5. University of Rhode Island

Department of Chemistry (Yang)

There is no change in personnel this quarter.

6. Montclair State College

Department of Chemistry (Humphrey)

During this period Dr. Humphrey had the help of two undergraduate research assistants, Heidi Weiss and Michael Ciarello. They utilized equipment and chemicals purchased with URI funding.

VIII. Contractual Administration

1. Prime Contract - University of Pennsylvania

Funding for the second year of the contract (10/1/87 to 9/30/88) has not been received as of 12/31/87. However, the University of Pennsylvania, after confirmation of the continuation of the contract from ONR, has agreed to advance money to the project to continue research. The University will not, however, issue modifications to the subcontracts on this project until the funding notice is received from ONR.

IX. Fiscal Status
Expenditures and Commitments

A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	Budgeted 9/15/86-9/30/87	Budgeted 10/1/87-9/30/88	Total Spent & Committed 9/15/86-12/31/87	Available Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	585,872	555,894	757,022
U of P (MSE) (Dr. G.C. Farrington)	231,565	309,845	359,287	182,123

B. Subcontracts

	Budgeted 9/15/86-9/30/87	Budgeted 10/1/87-9/30/88	Total* billed to date	Available Balance
OSU (Dr. A.J. Epstein)	867,116	369,597	844,237	392,476
Lockheed (Dr. T. Kuan)	87,037	87,037	97,152	76,922
MM Inc. (Ms. M. Dolton)	37,143	21,985	42,827	16,301
Academic Sub- Contractors				
a. Dr. Wnek				
1. MIT	36,996	0	36,796	200
2. RPI	36,006	69,940	20,279	85,667
b. Univ Rhode Island (Dr. S. Yang)	31,862	31,862	31,862	31,862
c. Montclair State (Dr. B. Humphrey)	29,231	31,862	29,231	31,862

*Represents monies paid on receipt of demand (i.e., bills) from participating subcontracts.